Applied Catalysis B: Environmental 180 (2016) 1–5

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Visible-light-sensitive two-step overall water-splitting based on band structure control of titanium dioxide

Satoshi Tanigawa[a], Hiroshi Irie[b,c,*]

[a] Special Doctoral Program for Green Energy Conversion Science and Technology, Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, 4 3 11 Takeda, Kofu, Yamanashi 400 8511, Japan
[b] Clean Energy Research Center, University of Yamanashi, 4 3 11 Takeda, Kofu, Yamanashi 400 8511, Japan
[c] Japan Science and Technology Agency, CREST, 5 Sanbancho, Chiyoda-ku, Tokyo 102 0075, Japan

ARTICLE INFO

Article history:
Received 20 April 2015
Received in revised form 4 June 2015
Accepted 5 June 2015
Available online 9 June 2015

Keywords:
Titanium dioxide
Visible light
Overall water-splitting
Two-step excitation

ABSTRACT

Visible light-induced two-step overall water splitting was achieved by combining two types of photocatalysts, which were prepared by introducing foreign elements into titanium dioxide (TiO_2) with a controlled electronic band structure. Rutile and anatase TiO_2 were doped with chromium and tantalum to introduce visible-light sensitivity. Under irradiation with only visible light from a 420-nm LED lamp, the simultaneous liberation of hydrogen and oxygen with a molar ratio of ~2:1 was achieved with these two types of TiO_2-based photocatalysts in the presence of iodate ion/iodide ion as a redox mediator.

1. Introduction

Various photocatalytic materials have been evaluated for water splitting activity because the generated hydrogen (H_2) represents a clean and renewable fuel source [1–4]. Among examined materials, titanium dioxide (TiO_2), with which Fujishima and Honda first demonstrated photoinduced water-splitting [1], is the most promising photocatalyst due to its abundance, nontoxicity, thermal stability and high resistance against photo-corrosion. Despite these advantageous properties, TiO_2 is only sensitive to ultraviolet (UV) light and therefore requires modification for the utilization of visible light. To this end, numerous studies have examined the effects of doping foreign elements into TiO_2 on visible-light induced water-splitting [5–7]. Although doped TiO_2 is able to generate either H_2 or oxygen (O_2) in the presence of sacrificial agents following irradiation with visible light (half reaction of water-splitting), the simultaneous generation of H_2 and O_2 from water in stoichiometric amounts (overall water-splitting) has not been achieved to date.

Several photocatalysts are capable of overall water-splitting under visible-light irradiation when combined with an appropriate cocatalyst and include gallium nitride (GaN)-zinc oxide (ZnO) solid-solution [4,8–10], zinc-germanium oxynitride ($(Zn_{1.44}Ge)(N_2O_{0.44})$) [11], bismuth-yttrium-tungsten ternary oxide ($BiYWO_6$) [12], niobium-substituted silver-tantalum oxide ($AgTa_{0.7}Nb_{0.3}O_3$) [13], and nano-particulate CoO [14]. Combined systems consisting of two specific photocatalysts for H_2 and O_2 production and a suitable redox couple can also function as visible-light sensitive photocatalysts for overall water-splitting (two-step overall water-splitting or Z-scheme overall water-splitting) [15–17]. Recently, our group [18] and Maeda et al. [19] successfully synthesized a combined system consisting of only one mother material, strontium titanate ($SrTiO_3$)-based and tantalum oxynitride (TaON)-based photocatalysts, respectively. Based on the activities of these systems, it is conceivable that visible-light-sensitive two-step overall water-splitting systems could be constructed by combining only TiO_2-based materials doped with appropriate metal ions. Based on evidence in the literature, chromium (Cr) 3d forms an isolated band in the forbidden band above the valence band (VB) and below the conduction band (CB) of anatase and rutile TiO_2, respectively when Cr^{3+} is doped at a Ti^{4+} site [20,21]. Thus, Cr-doped anatase and rutile TiO_2 are expected to function as the H_2- and O_2-production photocatalysts, respectively.

Here, tantalum ion (Ta^{5+}) was utilized as a counter dopant to Cr^{3+} at Ti^{4+} sites of anatase and rutile TiO_2 to maintain charge neutrality. Using this approach to combine Cr- and Ta-codoped TiO_2 photocatalysts in both the anatase and rutile forms, we achieved two-step overall water splitting under visible-light irradiation.

* Corresponding author. Fax: +81 55 220 8092.
E-mail address: hirie@yamanashi.ac.jp (H. Irie).

http://dx.doi.org/10.1016/j.apcatb.2015.06.008
0926-3373/

2. Experimental

2.1. Preparation of TiO_2-based photocatalysts

Cr/Ta-codoped anatase TiO_2 (Cr,Ta-TiO_2(A)) as a H_2-evolution photocatalyst was prepared by a hydrothermal synthesis method using commercial $Ti(SO_4)_2$ (24.0% purity, 1.92×10^{-2} mol; Kanto Kagaku), $CrCl_3 \cdot 6H_2O$ (93.0%, 4.00×10^{-4} mol; Kanto Kagaku), and $TaCl_5$ (4.00×10^{-4} mol; Kanto Kagaku) as starting materials. For the preparation of Cr/Ta-codoped rutile TiO_2 (Cr,Ta-TiO_2(R)) as an O_2-evolution photocatalyst, $Ti(SO_4)_2$ (1.96×10^{-2} mol), $CrCl_3 \cdot 6H_2O$ (1.80×10^{-4} mol), and $TaCl_5$ (1.80×10^{-4} mol) were utilized as the starting materials. The starting materials for the forms of TiO_2 were mixed and stirred in distilled water for 30 min using a magnetic stirrer. The solutions were treated hydrothermally in an autoclave at 140 °C for 12 h, and the resulting mixtures were washed with sufficient distilled water, collected by centrifugation, and dried at 80 °C overnight. The dried mixtures were calcined at 600 °C for 12 h for the anatase form and 900 °C for 24 h for the rutile form, and were then thoroughly ground using a mortar and pestle. As references, non-doped anatase (TiO_2(A)) and rutile (TiO_2(R)) were prepared under identical conditions using only $Ti(SO_4)_2$.

The deposition of platinum (Pt) co-catalyst onto the synthesized Cr,Ta-TiO_2(A) and Cr,Ta-TiO_2(R) photocatalysts was performed by a photo-deposition method. Briefly, 0.5 g of Cr,Ta-TiO_2(A) or Cr,Ta-TiO_2(R) powder was first dispersed in 100 mL methanol solution (20 vol%) as a hole scavenger. The amount of $H_2PtCl_6 \cdot 6H_2O$ (98.5% purity; Kanto Kagaku) as the source of Pt needed to give a weight fraction of Pt relative to either Cr,Ta-TiO_2(A) or Cr,Ta-TiO_2(R) of 1×10^{-3} was calculated and then added to the aqueous suspensions of each dispersed photocataslyst. The suspensions were then sufficiently deaerated using liquid nitrogen (N_2). While deaerating the suspensions, a xenon (Xe) lamp (LA-251 Xe; Hayashi Tokei) equipped with an optical filter (Y-44, Hoya) was employed for light irradiation of the suspension for 4 h. The suspension was then centrifuged, washed with distilled water, and the resulting residues were dried at 80 °C overnight. The residues were ground into a fine powder using an agate mortar to obtain the Pt-deposited Cr,Ta-TiO_2(A) (Pt/Cr,Ta-TiO_2(A)) and Cr,Ta-TiO_2(R) (Pt/Cr,Ta-TiO_2(R)) photocatalyst powders. Pt deposition on TiO_2(A) (Pt/TiO_2(A)) and TiO_2(R) (Pt/TiO_2(R)) was also performed by the same procedure, except the Xe lamp was used without an optical filter.

2.2. Characterizations

The crystal structures of the prepared powders were examined by X-ray diffraction (XRD) using a PW-1700 system (Panalytical). UV–vis absorption spectra were obtained by the diffuse reflection method using a V-650 (JASCO) spectrometer. Quantitative analyses were performed by X-ray fluorescence (XRF) using a ZSXP Primus II system (Rigaku).

2.3. Photocatalytic water-splitting tests

Two types of photocatalytic water-splitting tests were performed in a gas-closed-circulation system, which was filled with argon gas (50 kPa) after deaeration. The amounts of evolved H_2 and O_2 were monitored using an online gas chromatograph (GC-8A; Shimadzu). Each time we performed the water-splitting experiments, a different amount of N_2 was detected. In addition, we repeatedly deaerated this system to a final pressure of 2.5 Pa and then introduced argon gas into the system in the same way. For these reasons, we considered that the detection of N_2 originated from the intruded air from outside, and the effect of residual O_2 (and N_2) in water was possibly excluded [13,18]. Thus, if N_2 was detected, the O_2 amount was calculated using the following equation: O_2 = obs. O_2 – (obs. N_2/0.78) × 0.21.

(1) Half reactions of water-splitting: H_2 and O_2 evolution was monitored in the presence of Pt/Cr,Ta-TiO_2(A) or Pt/Cr,Ta-TiO_2(R) (60 mg each) with the aid of iodide ion (I^-) (sodium iodide (NaI), 99.5% purity, 0.01 mol/L Kanto Kagaku) or iodate ion (IO_3^-) (sodium iodate ($NaIO_3$), 99.5% purity, 0.01 mol/L; Kanto Kagaku), respectively, as a sacrificial agent. The examinations were conducted in 10 mL of solution, without adjusting the pH, with constant stirring using a magnetic stirrer and under irradiation with visible light generated from a light-emitting diode (LED) lamp with a wavelength of 420 nm (420-nm LED, LEDH60-420, Hamamatsu Photonics).

(2) Two-step overall water splitting: Photocatalytic overall water-splitting experiments were conducted by adding the sample powders (Pt/Cr,Ta-TiO_2(A): 90 mg, Pt/Cr,Ta-TiO_2(R): 10 mg) to 10 mL I^-/IO_3^- solutions (I^-: 8 mL, IO_3^-: 2 mL) as redox mediators. The suspension was constantly stirred using a magnetic stirrer and the pH was not adjusted. The 420-nm LED light was used for light irradiation. As references, the water-splitting experiments were performed under the identical conditions with 90 mg of Cr,Ta-TiO_2(A) in place of Pt/Cr,Ta-TiO_2(A) and 10 mg of Pt/Cr,Ta-TiO_2(R) as well as with 90 mg of Pt/Cr,Ta-TiO_2(A) and 10 mg of Pt/TiO_2(R) in place of Pt/Cr,Ta-TiO_2(R), in addition to 90 mg of Pt/TiO_2(A) and 10 mg of Pt/TiO_2(R).

2.4. Isotope labeled-water splitting

Photocatalytic overall water-splitting tests were also conducted with the Pt/Cr,Ta-TiO_2(A) and Pt/Cr,Ta-TiO_2(R) powders suspended in 10 mL of I^-/IO_3^- solution containing 30% isotopic water ($H_2{}^{18}O$, purity, 97 atom% ^{18}O; Sigma-Aldrich,) under the same conditions as above. Evolved gas was detected by a gas chromatograph mass spectrometer (GCMS, GCMS-QP 2010 Ultra, Shimazu) operated in selective-ion mode to monitor for 28 (N_2), 32 ($^{16}O^{16}O$), 34 ($^{16}O^{18}O$), and 36($^{18}O^{18}O$) ions. Spectra were measured under the same conditions used for two-step overall water splitting tests. Natural isotopic compositions of ^{16}O, ^{17}O, and ^{18}O are 99.757, 0.038, and 0.205 atm%, respectively [22]. Then, the compositions of $^{32}O_2$ ($^{16}O^{16}O$), $^{34}O_2$ ($^{16}O^{18}O$, $^{17}O^{17}O$), and $^{36}O_2$ ($^{18}O^{18}O$) in the atmospheric condition are calculated to be 99.515, 0.409, and 0.000420 atm%, respectively. We plotted the calculated $^{16}O^{18}O$ and $^{18}O^{18}O$ values using the following equation provided that the $^{14}N^{14}N$ was observed as the result of air contamination from outside as mentioned above: $^{16}O^{18}O$ = obs. $^{16}O^{18}O$ – (obs. $N_2 \times 0.21/0.78) \times 0.409 \times 10^{-2}$, and $^{18}O^{18}O$ = obs. $^{18}O^{18}O$ – (obs. $N_2 \times 0.21/0.78) \times 0.000420 \times 10^{-2}$ (in fact, $^{18}O^{18}O$ was considered to be equal to obs. $^{18}O^{18}O$ due to the extremely small value of 0.000420×10^{-2}).

3. Results and discussion

3.1. Characterization of the prepared photocatalysts

Elemental analyses by XRF indicated that the molar ratios of Ti: Cr: Ta in Pt/Cr,Ta-TiO_2(A) were 0.982: 0.004: 0.014 and those of Ti: Cr: Ta in Pt/Cr,Ta-TiO_2(R) were 0.992: 0.002: 0.006. Notably, these molar ratios were not consistent with the starting ratios used in the preparation of the photocatalysts. This discrepancy was attributed to differences in the solubility of Ti, Cr and Ta in aqueous solution under hydrothermal conditions. The analyses also indicated that the molar fractions of Pt relative to Cr,Ta-TiO_2(A) and Cr,Ta-TiO_2(R) were 9×10^{-4} and 5×10^{-4}, respectively. Cr,Ta-TiO_2(A) and Cr,Ta-TiO_2(R) were confirmed to have a single phase of anatase and rutile TiO_2, respectively, in the obtained XRD spectra (Fig. 1a). In addition, the XRD peaks of Cr,Ta-TiO_2(A) and Cr,Ta-TiO_2(R) were shifted

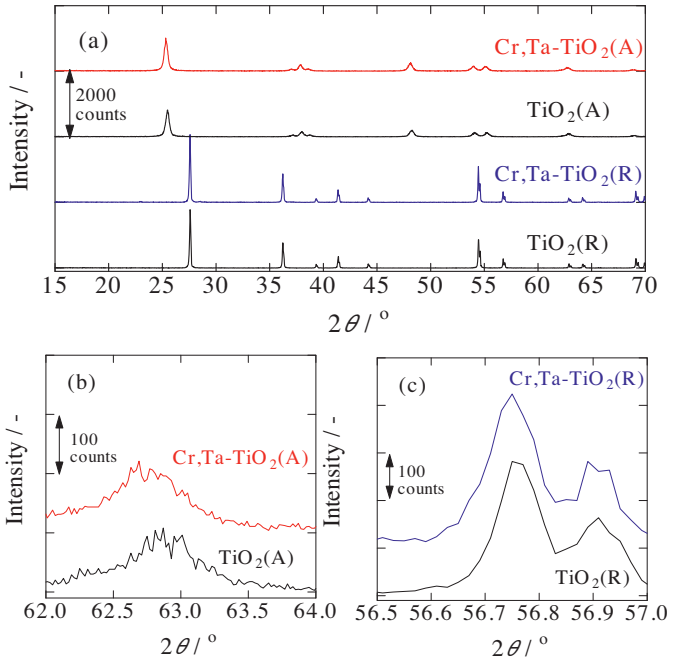


Fig. 1. XRD patterns of prepared TiO_2(A), Cr,Ta-TiO_2(A), TiO_2(R), and Cr,Ta-TiO_2(R) powders (a)–(c) are enlargements of (a).

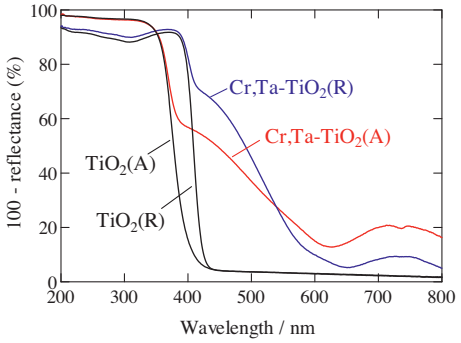


Fig. 2. UV-visible absorption spectra of TiO_2(A), Cr,Ta-TiO_2(A), TiO_2(R), and Cr,Ta-TiO_2(R).

to a lower 2θ angle compared to non-doped TiO_2(A) and TiO_2(R) (Figs. 1b and 1c). These results are reasonable when one considers that the effective ionic radii of Ti^{4+}, Cr^{3+}, and Ta^{5+} (six-coordination) are 0.0605, 0.0615, and 0.064 nm, respectively [23]. Thus, in both the anatase and rutile forms of the TiO_2 photocatalysts, Cr and Ta ions were likely incorporated at Ti sites.

The UV-visible absorption spectra of TiO_2(A), Cr,Ta-TiO_2(A), TiO_2(R), and Cr,Ta-TiO_2(R) were measured using a diffuse reflection method (Fig. 2). In the spectra of both Cr,Ta-TiO_2(A) and Cr,Ta-TiO_2(R), an absorption shoulder in the visible-light region and a negligible shift of the absorption edges were observed compared to those of TiO_2(A) and TiO_2(R). These findings indicate that the band-gaps of Cr,Ta-TiO_2(A) and Cr,Ta-TiO_2(R) did not markedly differ from those of TiO_2(A) and TiO_2(R), respectively.

3.2. Half reactions of water-splitting

We next examined the evolution of H_2 and O_2 by Pt/Cr,Ta-TiO_2(A) and Pt/Cr,Ta-TiO_2(R) in the presence of I^- and IO_3^- as sacrificial agents, respectively, and under irradiation with visible light (> 420 nm). As shown in Fig. 3, H_2 evolution by Pt/Cr,Ta-TiO_2(A) was only detected for in the presence of I^-, and was not

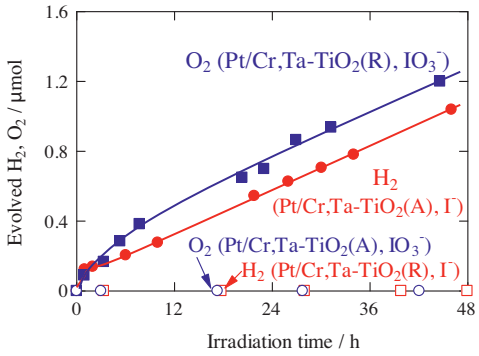


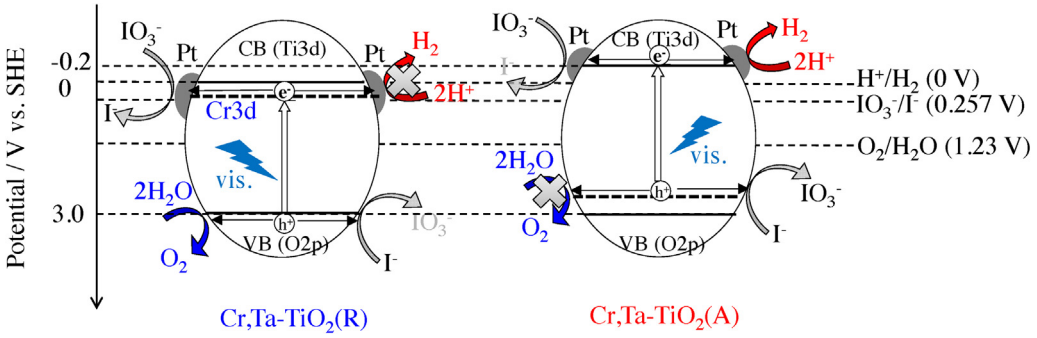
Fig. 3. Time courses of O_2 evolution resulting from the half water-reaction by Pt/Cr,Ta-TiO_2(R) photocatalyst irradiated with visible light (420-nm LED) in the presence of IO_3^- as a sacrificial agent. H_2 evolution was also monitored, but H_2 was not detected. Time courses of H_2 evolution by Pt/Cr,Ta-TiO_2(A) photocatalyst irradiated with visible light (420-nm LED) in the presence of I^- as a sacrificial agent. O_2 evolution was also measured, but was not detected.

observed in the system with Pt/Cr,Ta-TiO_2(R). In contrast, O_2 evolution was only detected for Pt/Cr,Ta-TiO_2(R) in the presence of IO_3^-, and did not proceed for Pt/Cr,Ta-TiO_2(A). Thus, we could confidently conclude that the introduced Cr 3d orbital in Cr,Ta-TiO_2(A) was responsible for the oxidation of I^- and was not involved in O_2 evolution, whereas the CB of Cr,Ta-TiO_2(A) was responsible for H_2 evolution under irradiation with visible light. In contrast, the introduced Cr 3d orbital in Cr,Ta-TiO_2(R) was responsible for the reduction of IO_3^- and was not involved in the evolution of H_2, whereas the VB of Cr,Ta-TiO_2(R) was responsible for O_2 evolution under irradiation with visible light. From these experimental results, in combination with the UV-visible absorption spectra, we confirmed that Cr 3d forms an isolated band above the VB in Cr,Ta-TiO_2(A) and below the CB of Cr,Ta-TiO_2(R) (Scheme 1). Although the potential of Cr 3d orbital in Cr,Ta-TiO_2(A) is lower than the O_2/H_2O potential (1.23 V vs. SHE), O_2 evolution was not observed. This is plausible when we consider the overpotential for O_2 evolution. To reduce the overpotential, intensive studies to investigate a cocatalyst that can reduce the overpotential have been performed by mimicking O_2-evolving centers in photosystem II in artificial photosynthetic systems [24–26]. If such a cocatalyst is grafted on the surface of Cr,Ta-TiO_2(A), it would be able to oxidize water to produce O_2.

3.3. Two-step overall water splitting

We examined water splitting by the Pt/Cr,Ta-TiO_2(A) and Pt/Cr,Ta-TiO_2(R) photocatalysts under visible-light irradiation (420-nm LED) for 500 h in the presence of IO_3^-/I^- as a redox mediator (Fig. 4). As shown in Fig. 4a, the levels of H_2 and O_2 increased in a linear manner with increasing irradiation time and repeated evacuations of the system. Notably, H_2 to O_2 were evolved at similar levels in nearly stoichiometric (~2–1) amounts during each irradiation cycle. These results demonstrate that overall water-splitting was achieved in this system.

In contrast to the combination of bare Cr,Ta-TiO_2(A) and Pt/Cr,Ta-TiO_2(R), and IO_3^-/I^- as a redox mediator in the system, trace amounts of O_2 were produced under irradiation with visible light (420-nm LED), but H_2 was not detected (Fig. 4b). This result indicates that Pt on Cr,Ta-TiO_2(A) functions as the site of H_2 evolution. As determined by XRF analysis, the Pt/Cr,Ta-TiO_2(A) sample contained Pt at a molar percentage of 9×10^{-4} (0.09 mol%). Therefore, because a total of 90 mg of the Pt/Cr,Ta-TiO_2(A) sample was used in the water-splitting experiment, the amount of Pt was 0.98 μmol. As the total amount of H_2 generated during the 500-h experiment was 1.12 μmol, we estimated that the turnover



Scheme 1. Schematic illustrations of the half-reaction of water splitting, O_2 evolution over Pt/Cr,Ta-TiO_2(R) photocatalyst irradiated with visible light (420-nm LED) in the presence of the sacrificial agent IO_3^-, and H_2 evolution over Pt/Cr,Ta-TiO_2(A) photocatalyst irradiated with visible light (420-nm LED) in the presence of I^- as a sacrificial agent.

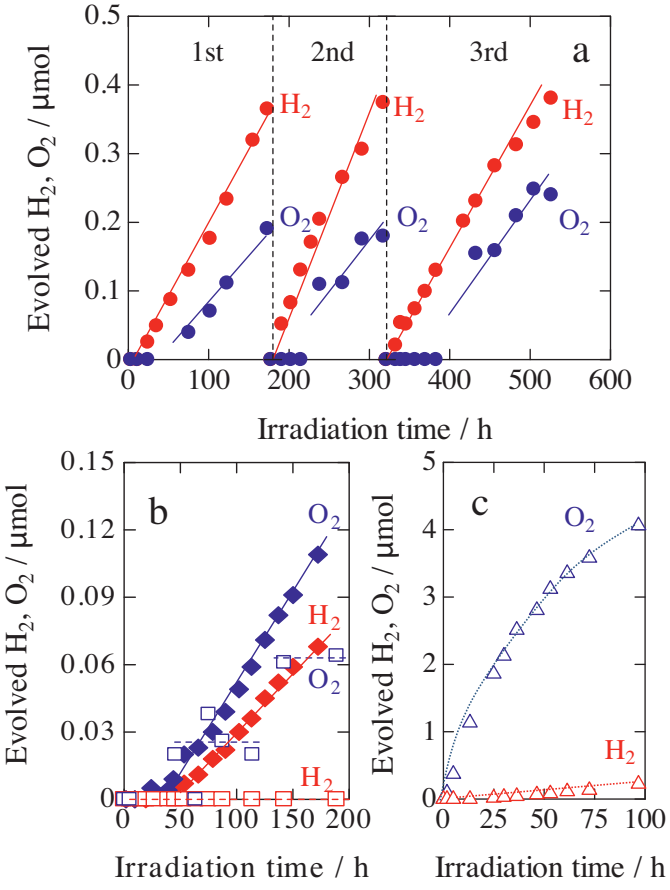
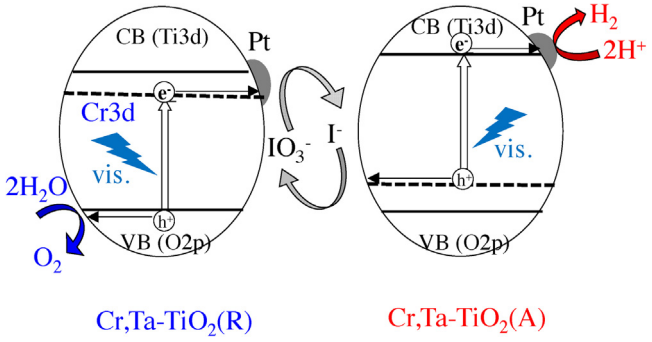


Fig. 4. (a) Time courses of H_2 and O_2 evolution resulting from photocatalytic water-splitting by Pt/Cr,Ta-TiO_2(A) and Pt/Cr,Ta-TiO_2(R) under irradiation with visible light (420-nm LED). The reaction was allowed to proceed for 500 h with twice evacuations of the system. (b) The time courses of H_2 and O_2 evolution for Cr,Ta-TiO_2(A) and Pt/Cr,Ta-TiO_2(R) photocatalysts (open squire) and for Pt/Cr,Ta-TiO_2(A) and Pt/TiO_2(R) photocatalysts (closed rhombus) irradiated with visible light (420-nm LED). (c) H_2 and O_2 evolution by Pt/TiO_2(A) and Pt/TiO_2(R) photocatalysts irradiated with visible light (420-nm LED).



Scheme 2. Schematic illustrations of spontaneous H_2 and O_2 evolution over Pt/Cr,Ta-TiO_2(A) and Pt/Cr,Ta-TiO_2(R) photocatalysts irradiated with visible light (420-nm LED) in the presence of IO_3^-/I^- redox mediator.

number, the ratio of total amount of produced to H_2 to that of Pt co-catalyst, was 1.14, which exceeded 1, indicating that this reaction proceeded catalytically.

It should be noted that in the system with Pt/TiO_2(A) and Pt/TiO_2(R) under identical conditions as those used for the above water-splitting experiments, a large amount of O_2 was produced due to the half-reaction of Pt/TiO_2(R) in the presence of IO_3^- acting as the sacrificial agent, resulting in a large deviation from the stoichiometric ratio of H_2 and O_2 evolution (Fig. 4c). Moreover, in the system with Pt/Cr,Ta-TiO_2(A) and Pt/TiO_2(R) under identical conditions, simultaneous H_2 and O_2 were evolved; however they were extremely small amounts at the non-stoichiometric ratio (Fig. 4b). Thus, the introduced Cr 3d orbitals in the Cr,Ta-TiO_2(A) and Cr,Ta-TiO_2(R) photocatalysts play an important role in generating H_2 and O_2 in stoichiometric amounts.

Taking Scheme 1 and the results presented in Fig. 4a and b into consideration, we propose a probable mechanism for overall water splitting by Pt/Cr,Ta-TiO_2(A) and Pt/Cr,Ta-TiO_2(R), as schematically illustrated in Scheme 2. In this model, visible light-excited electrons in the CB of Cr,Ta-TiO_2(A) are thought to reduce H_2O and generate H_2, whereas holes in the VB of Cr,Ta-TiO_2(R), which oxidize H_2O to produce O_2. In addition, visible-light-excited holes in the isolated Cr 3d state of Cr,Ta-TiO_2(A) and electrons in the isolated Cr 3d state contribute to the turn-over of I^- to IO_3^- and IO_3^- to I^-, respectively.

3.4. Isotope labeled-water splitting

To confirm the production of O_2 from water by this system under visible-light irradiation (420-nm LED), we examined water splitting using water containing 30% $H_2{}^{18}O$ (Fig. 5). As N_2 was unexpectedly detected, $^{16}O^{16}O$ was not included in the analysis, which was therefore limited to $^{16}O^{18}O$ and $^{18}O^{18}O$. We could repeatedly detect $^{16}O^{18}O$ and $^{18}O^{18}O$ following irradiation of the system with 420-nm light, but did not detect $^{18}O^{18}O$ under dark conditions. Although a small amount of $^{16}O^{18}O$ was observed under dark conditions, however the detected peak area was so small, causing the poor signal/noise (S/N) ratio. In addition, we couldn't have tendency to increase with increasing dark storage time. At the moment, we cannot confidently conclude whether $^{16}O^{18}O$ indeed formed or not. The $^{16}O^{18}O$ amount under dark conditions was much smaller than

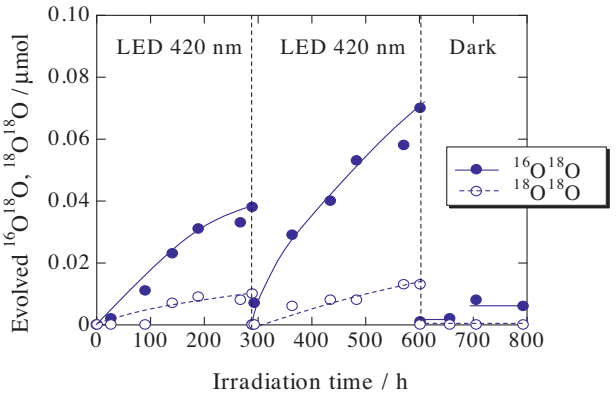


Fig. 5. Time courses of $^{16}O^{18}O$ and $^{18}O^{18}O$ evolution from water containing 30% $H_2{}^{18}O$ by Pt/Cr,Ta-TiO_2(A) and Pt/Cr,Ta-TiO_2(R) photocatalysts irradiated with visible light (420-nm LED). The reaction was allowed to proceed for 600 h with once evacuation. After a final evacuation of the system, the amount of $^{16}O^{18}O$ and $^{18}O^{18}O$ produced under dark conditions was also measured.

that detected in the system irradiated with 420-nm light. More importantly, $^{18}O^{18}O$ was detected under 420-nm light, whereas was not detected at all under dark conditions. Thus, it was confirmed that O_2 was liberated from water by the photocatalytic system under visible-light irradiation at 420 nm.

4. Conclusions

We established a two-step overall water-splitting system that is sensitive to visible light by utilizing two types of TiO_2-based photocatalysts that simultaneously evolve H_2 and O_2 at a molar ratio of ~2:1 in the presence of IO_3^-/I^-. However, because the evolution rates were not high, it is necessary to further enhance the visible-light sensitivity of these TiO_2-based materials by optimizing the concentrations and types of dopants or by preparing deficient-free doped TiO_2. We have recently developed a solid-state two-step overall water-splitting photocatalyst, in which the H_2- and O_2-evolution photocatalysts were connected via silver [27]. In this system, distilled water could be split without a redox mediator. The construction of solid-state systems using TiO_2-based photocatalysts may be advantageous for industrial and practical applications, as no chemicals are required as sacrificial agents.

Acknowledgements

We express gratitude to Mr. G. Newton for the careful reading of the manuscript.

References

[1] A. Fujishima, K. Honda, Nature 238 (1972) 37–38.
[2] J. Sato, N. Saito, H. Nishiyama, Y. Inoue, J. Phys. Chem. B 105 (2001) 6061–6063.
[3] H. Kato, K. Asakusa, A. Kudo, J. Am. Chem. Soc. 125 (2003) 3082–3089.
[4] K. Maeda, K. Teramura, D. Lu, T. Takata, N. Saito, K. Inoue, Y. Domen, Nature 440 (2006) 295.
[5] H. Kato, A. Kudo, J. Phys. Chem. B 106 (2002) 5029–5034.
[6] R. Niishiro, R. Konta, H. Kato, W.-J. Chun, K. Asakura, A. Kudo, J. Phys. Chem. C 111 (2007) 17420–17426.
[7] L. Li, J. Yan, T. Wang, Z.-J. Zhao, J. Zhang, J. Gong, N. Guan, Nature Commun. 6 (2015) 5881/1–5881/10.
[8] K. Maeda, T. Takata, M. Hara, N. Saito, Y. Inoue, H. Kobayashi, K. Domen, J. Am. Chem. Soc. 127 (2005) 8286–8287.
[9] K. Maeda, K. Teramura, T. Takata, M. Hara, N. Saito, K. Toda, Y. Inoue, H. Kobayashi, K. Domen, J. Phys. Chem. B 109 (2005) 20504–20510.
[10] K. Teramura, K. Maeda, T. Saito, T. Takata, N. Saito, Y. Inoue, K. Domen, J. Phys. Chem. B 109 (2005) 21915–21921.
[11] Y. Lee, H. Terashima, Y. Shimodaira, K. Teramura, M. Hara, H. Kobayashi, K. Domen, M. Yashima, J. Phys. Chem. C 111 (2007) 1042–1048.
[12] H. Liu, J. Yuan, W. Shangguan, Y. Teraoka, J. Phys. Chem. C 112 (2008) 8521–8523.
[13] N. Lei, M. Tanabe, H. Irie, Chem. Commun. 49 (2013) 10094–10096.
[14] L. Liao, Q. Zhang, Z. Su, Z. Zhao, Y. Wang, Y. Li, X. Lu, D. Wei, G. Feng, Q. Yu, X. Cai, J. Zhao, Z. Ren, H. Fang, F.R. -Hernandez, S. Baldelli, J. Bao, Nature Nanotech. 9 (2014) 69–73.
[15] K. Sayama, K. Mukasa, R. Abe, Y. Abe, H. Arakjawa, J. Photo. Photo. A 148 (2002) 71–77.
[16] H. Kato, Y. Sasaki, A. Iwase, A. Kudo, Bull. Chem. Soc. Jpn. 80 (2007) 2457–2464.
[17] A. Kudo, Int. J. Hydrogen Energy 32 (2007) 2673–2678.
[18] S. Hara, M. Yoshimizu, S. Tanigawa, L. Ni, B. Ohtani, H. Irie, J. Phys. Chem. C 116 (2012) 17458–17463.
[19] K. Maeda, R. Abe, K. Domen, J. Phys. Chem. Lett. 115 (2011) 3057–3064.
[20] T. Umebayashi, T. Yamaki, H. Itoh, K. Asai, J. Phys. Chem. Solids 63 (2012) 1909–1920.
[21] C. Di Valentin, G. Pacchioni, H. Onishi, A. Kudo, Chem. Phys. Lett. 469 (2009) 166–171.
[22] K.J.R. Rosman, P.D.P. Taylor, Pure Appl. Chem. 70 (1998) 217–235.
[23] R.D. Shannon, C.T. Prewitt, Acta Cryst. B 25 (1969) 925–946.
[24] M.W. Kanan, Y. Surendranath, D.G. Nocera, Chem. Soc. Rev. 38 (2009) 109–114.
[25] J. Suntivich, K.J. May, H.A. Gasteiger, J.B. Goodenough, Y.S. -Horn, Science 334 (2011) 1383–1385.
[26] T. Takashima, K. Hashimoto, R. Nakamura, J. Am. Chem. Soc. 134 (2012) 18153–18156.
[27] R. Kobayashi, S. Tanigawa, T. Takashima, B. Ohtani, H. Irie, J. Phys. Chem. C 118 (2014) 22450–22456.